Advanced Concepts for Vehicular Containment of Compressed and Cryogenic Hydrogen

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ABSTRACT:

LLNL is developing insulated pressure vessels with thermal endurance at least 5X longer than conventional liquid hydrogen (LH_2) tanks, and can eliminate evaporative losses in routine use. These pressure vessels can be fueled with ambient temperature H_2 and/or LH_2. When filled with LH_2, these vessels contain 2-3 times more fuel than compressed H_2 tanks at room temperature. LLNL has demonstrated the concept onboard an (L)H_2 fueled pickup truck. We are now working on a next generation vessel with much improved packaging characteristics. We are also researching three concepts for conformable pressure vessels to improve space utilization on vehicles: filament wound vessels using appropriate geometries to effectively cancel the bending stresses from internal pressure, as well as both macrolattice and replicant concepts that use an internal structure to resist pressure forces with a thin outer seal for H_2 containment. We are building and pressure testing first generation prototypes to investigate their potential for conformability.

***KEYWORDS: hydrogen storage, compressed hydroge*n, cryogenic hydrogen, pressure vessels**

INTRODUCTION

One of the fundamental hurdles to the widespread commercialization of hydrogen (H_2) vehicles is storing enough hydrogen on-board for a reasonable range (300-400 miles). Lawrence Livermore National Laboratory (LLNL) is working on two hydrogen storage concepts that may demonstrate an advantage over existing technologies. The first concept is an insulated pressure vessel which can store liquid hydrogen (LH_2) with dramatically improved thermal endurance, the main challenge facing conventional low pressure LH_2 tanks, for example those developed over the past 30 years by BMW [1]. In addition, insulated pressure vessels offer refueling and infrastructure flexibility since they can fill with ambient temperature compressed gaseous hydrogen (GH_2), to reduce fuel cost or energy intensity while expanding the number of potential refueling locations.

The second concept, conformable pressure vessels, can better occupy available space onboard the vehicle, minimizing cargo space intrusion. Radially symmetric (cylindrical or spherical) shapes are easiest for pressure vessel design, analysis and fabrication. However, available spaces inside a vehicle are typically not cylindrical or spherical. Conformable vessels extend vehicle range for a given space or pressure limitation.

INSULATED PRESSURE VESSELS

This concept consists of storing fuel in a vessel that can operate at cryogenic temperatures (20 K) *and* high pressures (e.g. up to 350 atm). This vessel can be fueled exclusively with LH_2, or it can be fueled flexibly with LH_2, cryogenic GH_2, or ambient temperature GH_2. By offering multiple refueling modes insulated pressure vessels present advantages with respect to conventional LH_2 and GH_2 vessels. (Figure 1).

Insulated Pressure Vessels Filled with LH_2: If the insulated pressure vessel is fueled with LH_2, it becomes a compact vessel that goes a long way toward solving the problems typically associated with LH_2 tanks: evaporative losses after a short period of inactivity, evaporative losses for short daily driving distances, and danger of being stranded due to fuel evaporation.

The dormancy (period of inactivity before a vessel releases hydrogen to reduce pressure build up) is an important parameter for LH_2 vehicle acceptability. Dormancy can be calculated from the first law of thermodynamics [2] and the properties of H_2 [3]. We have generated a thermodynamic phase diagram for hydrogen (Figure 2) that has features that make it especially useful for hydrogen dormancy calculations.

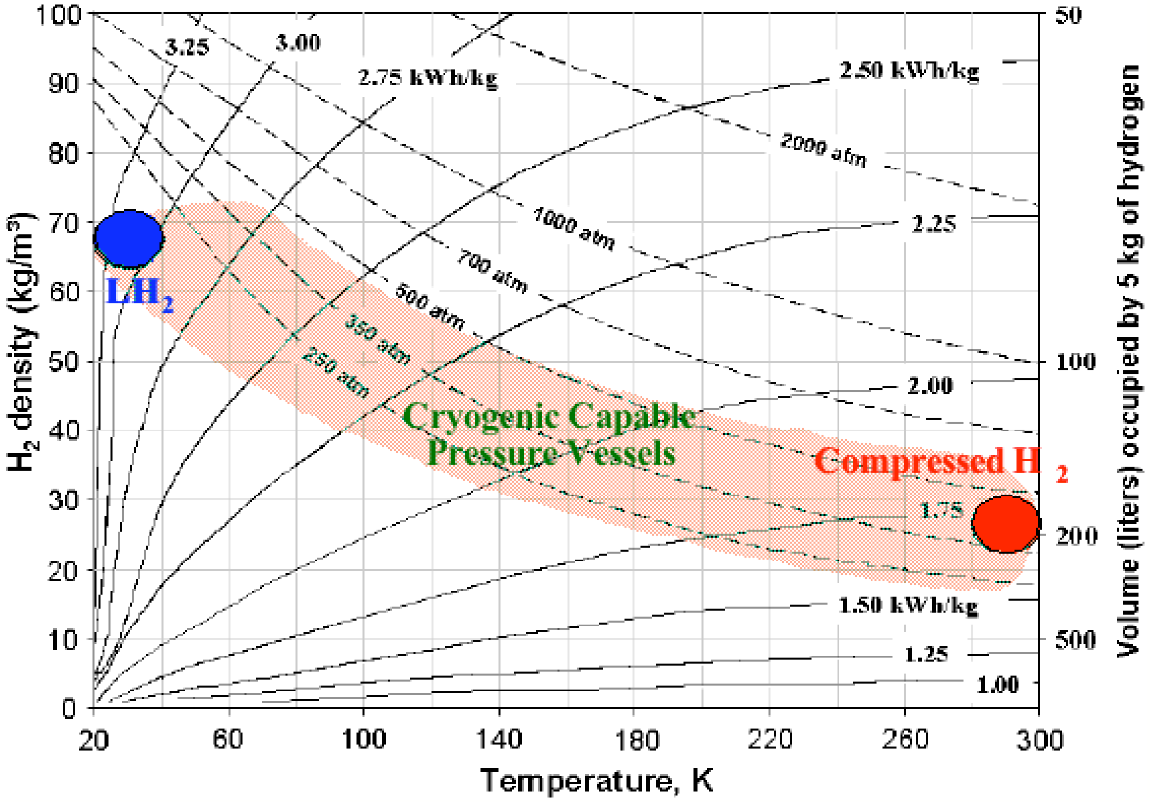


Figure 1. Commercial automotive hydrogen storage technologies occupy the extremes of this phase diagram. Hydrogen is often stored as a compressed gas, GH_2 (red dot) at ambient temperature (horizontal axis), very high pressure (dotted lines), and relatively low density (vertical axis). Hydrogen is stored at much higher density as a cryogenic liquid, LH_2 (blue dot) with higher energetic cost (solid lines indicate the theoretical minimum work, also known as thermomechanical exergy) to densify hydrogen. Insulated pressure vessels have flexibility to operate across a broad region (shaded in green) of the phase diagram, and therefore can be fueled with GH_2 at a low energetic cost when energy or fuel cost savings is important or with LH_2 when long driving range is a higher priority.

We start the dormancy calculation by identifying in Figure 2 the initial thermodynamic state (density and internal energy) of the hydrogen contained in the vessel. From this initial point, the thermodynamic state of the hydrogen in a parked vehicle moves horizontally to the right (warming at constant density) due to heat transfer from the environment, until the hydrogen pressure reaches the vessel maximum, and hydrogen has to be released. The cumulative thermal energy absorbed by the hydrogen while a car is parked can be calculated by multiplying the mass of the hydrogen in the vessel, by the total change in its specific internal energy. This is shown graphically in Figure 2 by the area under the horizontal line joining the initial and final points in the process. Dormancy can then be calculated by dividing the total heat absorbed (the area under the line) by the heat transfer rate.

The scales in Figure 2 have been appropriately chosen to simplify the dormancy calculations. The grid scale in the internal energy (horizontal) axis is set at 86.4 kJ/kg H_2, which can be converted to 1 Watt-day/kg H_2 (1 day=86,400 seconds). The grid scale in the vertical axis represents 1 kg H_2. Therefore, the area of a grid square represents 1 Watt-day of heating. The total heating (in Watt-days) can be easily calculated by counting the squares under the horizontal line representing the parking process. Dormancy is calculated by dividing the heating (in Watt-days) by the rate of heat transfer (in Watts).

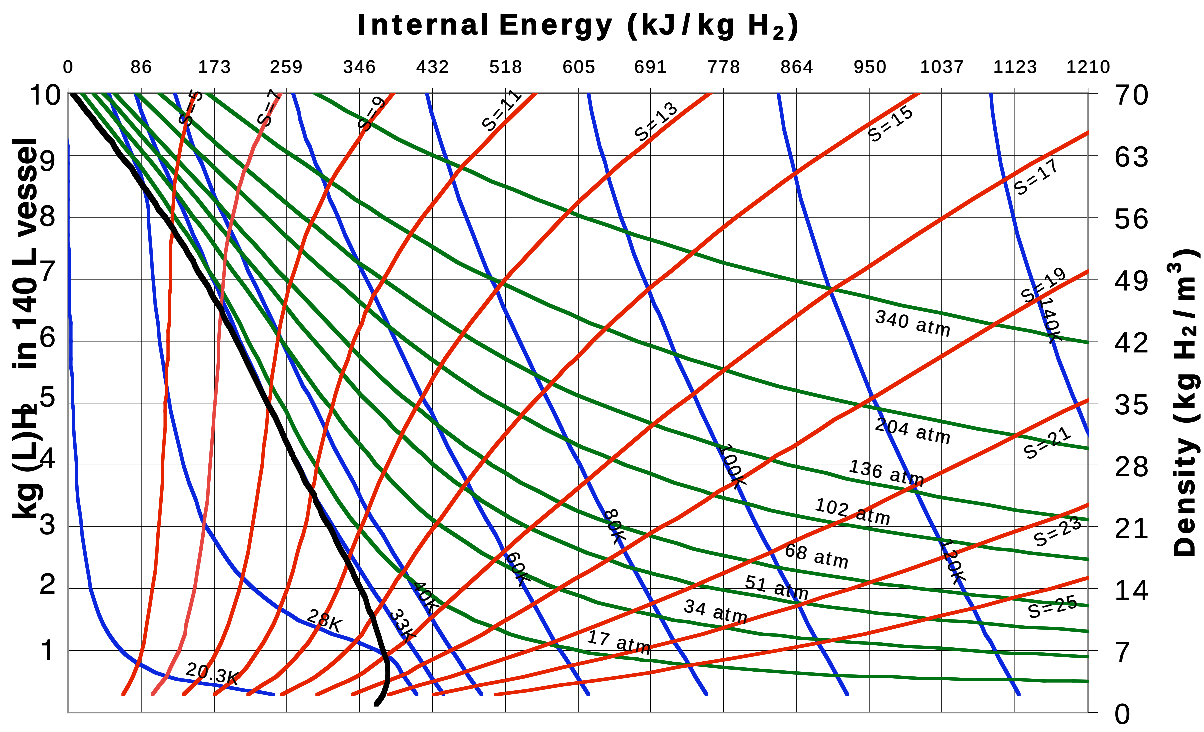


Figure 2. Phase diagram for hydrogen showing density (right vertical axis) and internal energy (horizontal axis), with lines for constant pressure (green), temperature (blue) and entropy (red). The figure also shows a thick black saturation line that separates the vapor phase (right) from the two phase liquid-vapor region (left). A second vertical axis in the left side shows the mass of hydrogen contained in a vessel with 140 liter internal volume, which would store 10 kg of LH_2 at 20 K and 1 bar.

Now, consider a conventional LH_2 tank with 140 liter internal volume and 6 bar maximum working pressure. Assume that the vessel is initially 80% full with 8 kg LH_2 at 20 K and 1 bar (Point 1 in Figure 3). The vehicle is then parked. As the hydrogen heats up, its temperature and pressure increase. When the pressure reaches 6 bar (Point 2), dormancy ends because hydrogen needs to be vented to maintain the pressure within acceptable limits. Total heating in the process from Point 1 to Point 2 can be calculated as 8 Watt-days by counting the number of squares in the area marked in green. Dormancy can then be calculated by dividing 8 Watt-days by the heat transfer rate (e.g. 4 days for a 2 Watt tank or 2 days for a 4 Watt tank).

Figure 3 illustrates the dormancy advantage of insulated pressure vessels. Assuming a 340 atm (5000 psi) vessel initially filled with 8 kg LH_2 at 1 atm and 20 K, the vehicle can remain parked until the pressure reaches 340 atm (Point 3 in the figure) without venting any hydrogen. Counting squares under the line joining Point 1 and Point 3 (green and red areas) we obtain 8+48=56 Watt-days, a factor of ~7 times greater thermal endurance than a conventional LH_2 tank.

Insulated pressure vessels provide an even greater dormancy advantage when the vehicle is driven. If the parked vehicle is driven when the hydrogen is at state 3 (Figure 3), and the drive consumes 2 kg of hydrogen, the hydrogen in the tank expands and cools as the vehicle is driven following a constant entropy line from Point 3 to Point 4, extending the thermal endurance of the vessel by an additional 48 Watt-days before any evaporative losses occur (at Point 5). Further driving substantially extends the dormancy period, virtually eliminating losses in routine use.

Figure 2 greatly simplifies analysis of any driving cycle that combines driving and parking periods of different lengths. Evaporative losses and dormancy are easily calculable given a driving schedule, vessel volume and thermal performance (i.e. heat transfer leak rate).

It must be noted that Figure 2 is conservative because it neglects the thermal capacity of the vessel as well as the conversion between the two different states of nuclear spin arrangement (*para*-hydrogen and *ortho*-hydrogen). Both of these effects tend to increase the dormancy of the vessels, and are most significant at warmer temperatures that may exist in insulated pressure vessels (T >80 K). Conventional LH_2 tanks operate at temperatures low enough (20-30 K) for both effects to be negligible.

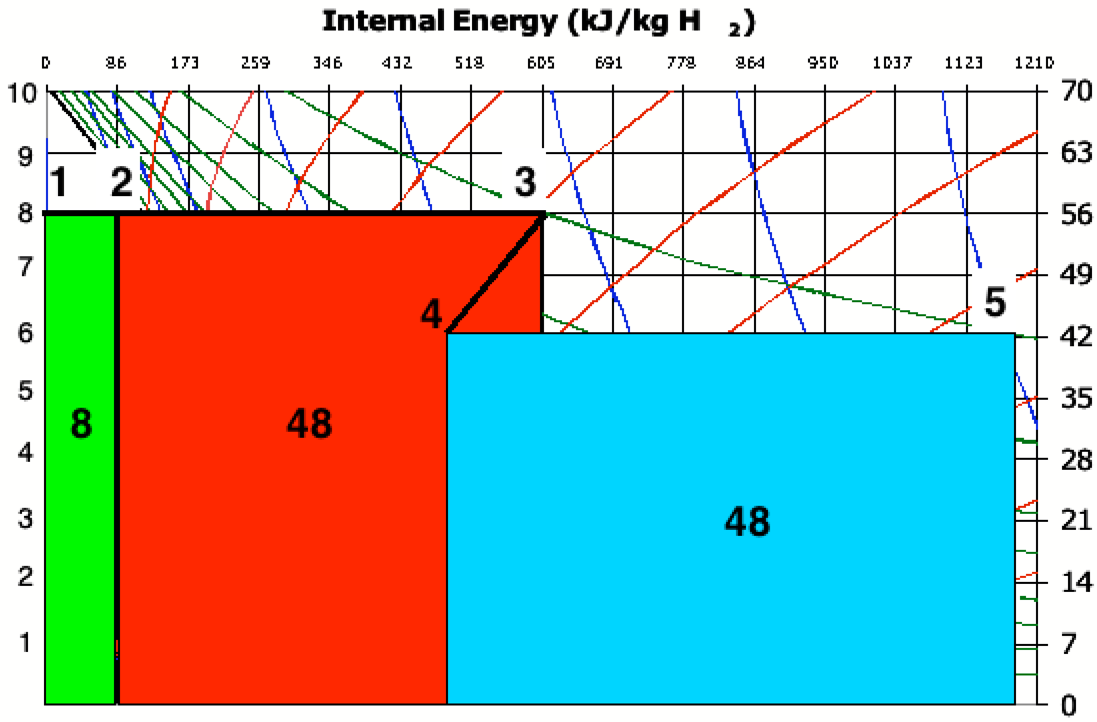


Figure 3. Phase diagram (repeated from Figure 2) with points and areas showing dormancy (in Watt-days) of conventional LH_2 tanks (green area) and insulated pressure vessels (green+red+blue areas).

Flexibly Fueling Insulated Pressure Vessels: The energy requirements for H_2 storage (compression and/or liquefaction) can be lower for a car with an insulated pressure vessel than for a car fueled exclusively with LH_2 storage because an insulated pressure vessel can use, but does not require, LH_2. An H_2 vehicle with 34 km/l (80 mpg) gasoline equivalent fuel economy using a 140 L, 340 atm insulated pressure vessel can achieve a 400 km range using ambient temperature GH_2, sufficient for the majority of trips. The additional energy, cost, and technological effort for cryogenic refueling need only be undertaken (and paid for) when greater range is needed for (infrequent) long trips. Use of compressed H_2 in all trips under 200 km (~85% of all the vehicle miles traveled in the USA [4]), would save 8 kWh_e/kg H_2, approximately 2/3 of the energy needed to store hydrogen on a vehicle that exclusively fills with LH_2 (neglecting evaporative losses from the conventional LH_2 tank).

The fuel cycle energy efficiency advantage of using ambient temperature GH_2 instead of LH_2 for short trips can be seen in Figure 1. Solid lines represent the theoretical minimum energy (the thermomechanical exergy [5]) necessary for compressing and cooling the hydrogen from ambient conditions (300 K and 1 atm) to any desired temperature and density. The figure also shows storage pressure in dotted lines. Ambient temperature compression is the most energy efficient method to densify H_2, since the theoretical (isothermal) work of compressing hydrogen rises only logarithmically with pressure. This trend is reflected in practice. Compressing GH_2 to 250-1000 atm theoretically requires 1.5-2.0 kWh/kg and 2.5-4.0 kWh/kg in practice, substantially less energy than conventional H_2 liquefaction (10-14 kWh/kg) [6, 7]. Electrolysis can generate H_2 at high pressure at near theoretical compression work efficiency [8].

Insulated pressure vessels operating with low temperature H_2 offer a dramatic and counterintuitive potential safety advantage compared to ambient temperature GH_2 storage. Figure 4 shows the maximum theoretical mechanical energy released by a sudden adiabatic expansion (e.g. in a vessel rupture) of high pressure hydrogen gas from three temperatures (80 K, 150 K and 300 K). A kilogram of H_2 stored at 70 atm and 300 K will release a theoretical maximum mechanical energy of 0.55 kWh if suddenly (i.e. adiabatically) expanded to atmospheric pressure (cooling substantially in the process). Counterintuitively, this maximum energy release increases only slightly if H_2 is stored at *much* higher pressures. Raising pressure from 70 atm to 1000 atm (1400% increase) increases the maximum (theoretical) mechanical energy release by only 10%, while shrinking vessel volume 83%, and strengthening (thickening) the vessel wall many times over. Over the likely range of onboard GH_2 storage pressures (350-1000 atm), the maximum mechanical energy release is nearly constant at 0.6 kWh per kg of GH_2. In sharp contrast, *temperature* has a very strong influence on theoretical burst energies. Cooling hydrogen gas from 300 K to 150 K and especially to 80 K reduces available mechanical energy by a factor of 2-6, mitigating the potential damage of a sudden rupture.

Technology Validation: We have built three generations of insulated pressure vessels, all incorporating a Type 3 (aluminum-lined, composite-wrapped) vessel. All designs include an outer vacuum vessel and multi-layer vacuum insulation to minimize heat transfer. The designs also include instrumentation for pressure and temperature as well as safety devices to prevent vessel rupture. The first generation subscale prototype stores about 1 kg of hydrogen. Six vessels of this design were built, and these prototypes were used for conducting DOT, ISO and SAE certification tests [9]. The vessels successfully met all the test criteria.

The second generation full scale prototype had a 9 kg LH_2 capacity within a 135 liter internal volume. Six vessels of this design were built, and five of them were used for additional certification testing. The sixth vessel was installed into a Ford Ranger pickup truck powered by a hydrogen internal combustion engine (Figure 5). The integration of the insulated pressure vessel into this vehicle required multiple changes to the fueling system to accommodate both LH_2 and GH_2. The truck was tested at Lawrence Livermore National Laboratory and SunLine Transit (Thousand Palms, California), refueled multiple times with LH_2 and GH_2, validating operation on both. Truck operating parameters, including driving distance, fuel use, fuel pressure, temperature, and fill level were continuously recorded in a computerized data acquisition system.

The third generation insulated pressure vessel (151 liter design, Figure 6) stores more fuel (10.7 kg LH_2) than the previous generation, in a total package that is considerably more compact. This design meets the US Department of Energy (DOE) 2007 volume target (1.2 kWh/liter) and the 2010 DOE weight target (2 kWh/kg). The vessel has a maximum pressure rating of 34.5 MPa (5000 psi), and will be installed in the trunk of a hydrogen powered Toyota Prius hybrid vehicle converted by Quantum, Inc. of Irvine, CA.

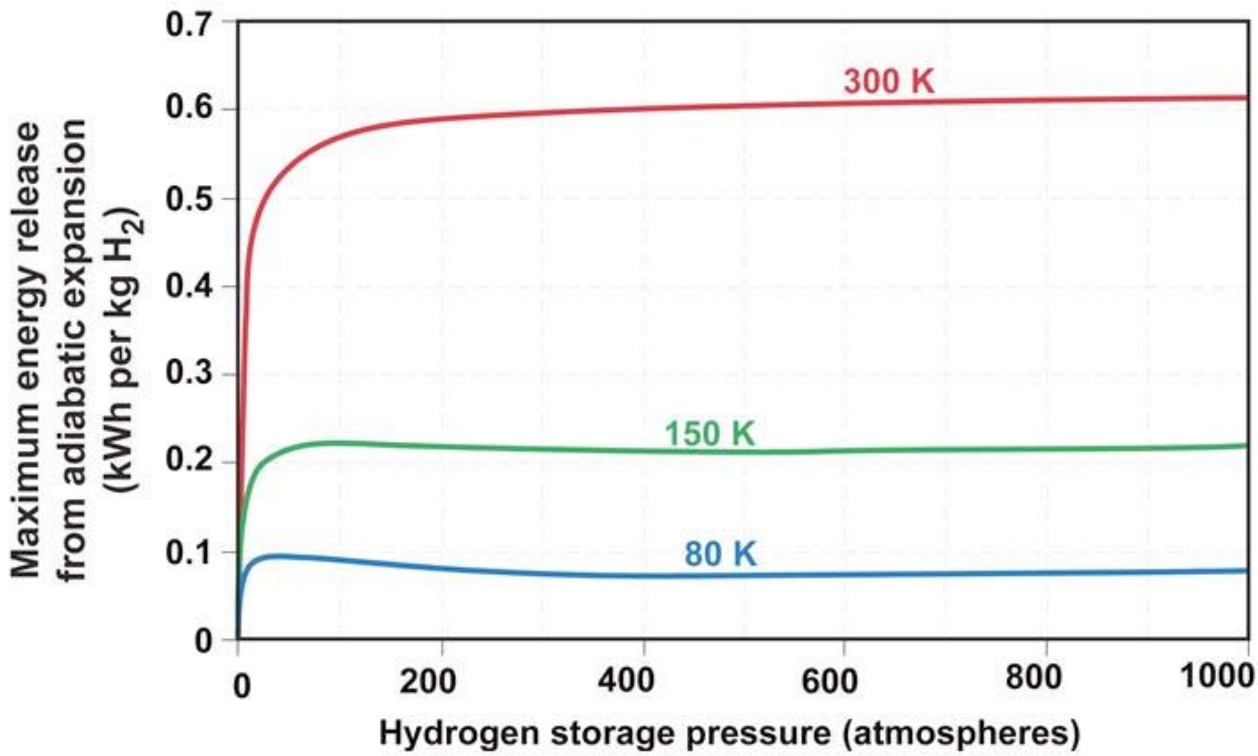


Figure 4. Maximum mechanical energy (per kilogram of hydrogen) released upon instantaneous expansion of H_2 gas (e.g. from a pressure vessel) as a function of initial storage pressure at 80 K, 150 K, and 300 K. For comparison, note that the chemical energy content of hydrogen is 33.3 kWh/kg. This mechanical energy is the theoretical maximum available work based on reversible *adiabatic* expansion from the pressure shown to 1 atm, calculated from internal energy differences of H_2 gas before and after isentropic expansion.

Figure 5. Hydrogen fueled 1992 Ford Ranger truck equipped with an insulated pressure vessel (3600 psi, 135 liter, 9 kg LH_2) demonstrated at Lawrence Livermore National Laboratory and by SunLine Transit at Thousand Palms, California.

Figure 6. Third generation insulated pressure vessel design with 151 L internal volume stores 10.7 kg of LH_2 and will be installed and demonstrated onboard a 2006 Toyota Prius converted by Quantum Inc. for hydrogen fuel use.

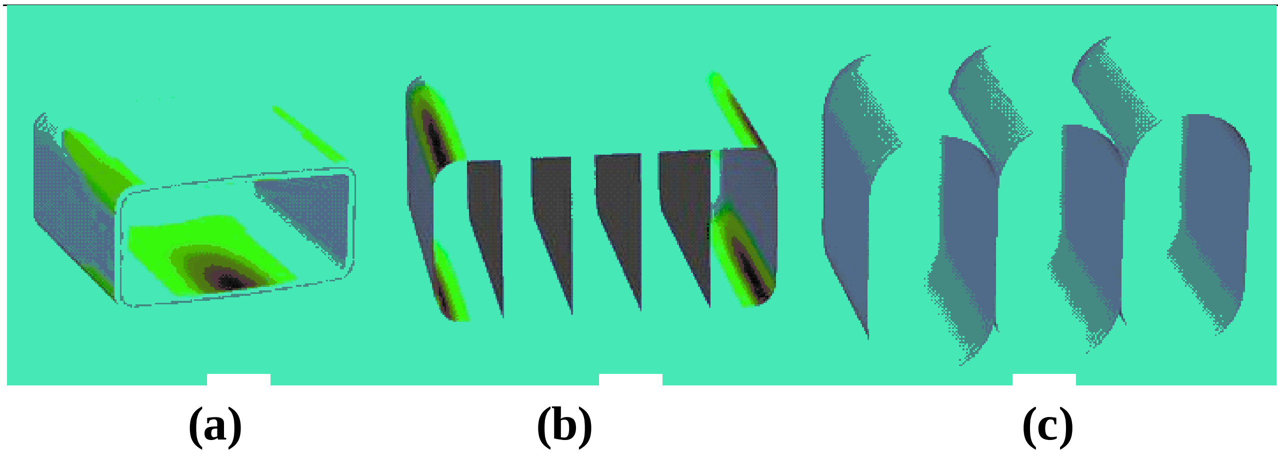


Figure 7. Three geometries selected for analysis of filament wound conformable high pressure vessels. (a) Sandwich, (b) ribbed, (c) pillow geometry. Colors in the figure indicate levels of stress calculated from finite element analysis.

CONFORMABLE PRESSURE VESSELS

Conformable vessels are another potential solution to the problem of vehicular hydrogen storage. Conformable tanks can be designed to better occupy available space in the vehicle, minimizing intrusion into the cargo space. Better utilization of available space in the vehicle is one way of extending vehicle range without dramatic changes to current vehicle designs. Between 20 and 40% improvements in range can be expected depending on the geometry of the available space and the level of conformability of the vessel.

Pressure vessels are typically cylindrical or spherical because these shapes are easiest for design, analysis and fabrication. However, available spaces inside a vehicle are typically not cylindrical or spherical. Optimum packaging efficiency is obtained by designing highly conformable vessels that can fill irregular spaces in the vehicle, adopting shapes similar to today's gasoline tanks. This, however, remains an extremely difficult task. As a first step toward delivering practical conformable vessels, we are working on designing vessels that better fill the square or rectangular spaces that are often available in vehicles. One reasonable figure of merit for conformable vessels is the "box" volumetric efficiency, defined as the internal volume of the vessel divided by the volume of the rectangular box that encloses the vessel.

The challenge of conformable vessels is managing mechanical bending forces. In cylindrical or spherical vessels, wall elements operate under pure tension with no bending. Cylindrical and spherical vessels may expand as they are pressurized, but they do not change shape. As soon as a vessel deviates from a cylindrical or spherical shape, it is subjected to bending stresses that may reduce the working pressure to impractical values. Pressurization also tends to modify the shape of a conformable vessel. Conformable pressure vessels need to be designed to minimize the effect of these bending stresses.

We are pursuing three parallel paths toward conformability: filament wound vessels, macrolattices and replicants. These concepts are described in the next paragraphs.

Filament Wound Conformable Vessels: We have explored three concepts for filament wound conformable pressure vessels (Figure 7). These concepts are titled the sandwich construction, the ribbed construction and the pillow construction.

The sandwich construction uses two parallel layers of composite fiber separated by a foam material that can transmit shear stresses between the inner layer and the outer layer, thereby reducing bending stresses to a manageable level. However, our finite element analysis revealed that the sandwich design was not appropriate for making viable conformable pressure vessels. The reason is that the fiber can transmit shear stresses but it cannot support the inner layer of composite as it tries to expand due to internal pressure. This results in very high bending stresses in the middle section of the inner composite.

The ribbed design can reduce the bending stresses to a manageable level, even though some stress concentration still exists at the corners (Figure 7). The issue with ribbed vessels is manufacturability, because it is difficult to properly attach the ribs to the outer skin of the vessel. Further work on evaluation of possible bonding and construction methodologies is necessary to deliver on the promise of this design.

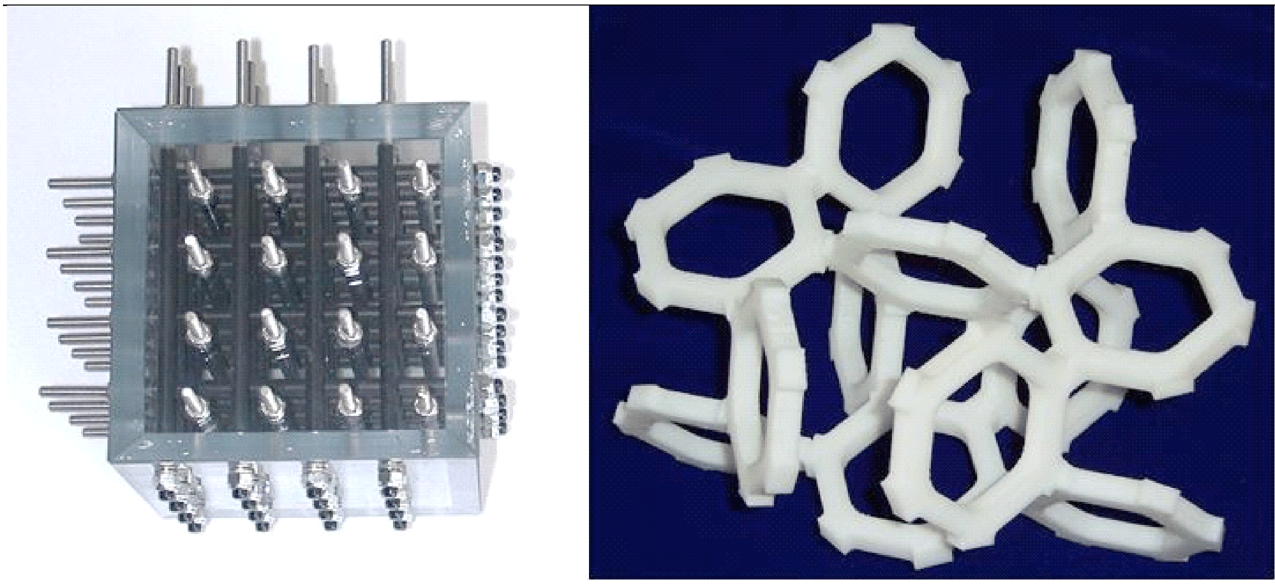
The pillow vessel consists of a series of flat sided segments with ellipsoidal edges (pillows). In this geometry, pressure exerts equal and opposite forces on the flat surfaces (as long as segments are kept at equal pressure). This has the important consequence of eliminating pressure forces (and bending stresses) on the flat surfaces. In addition to the pillow segments, this vessel design requires the manufacture of end segments that have a flat end and an elliptical end (not shown in Figure 7), to guarantee pressure elimination in all the flat surfaces. This geometry has been extensively analyzed with a finite element code, and the results have indicated good performance and little sensitivity to manufacturing defects. Figure 7 shows a very uniform stress distribution with no stress concentration anywhere in the vessel.

The promise of the “pillow tank” concept is being researched both analytically and experimentally. We have built and pressure tested two prototype pillow segments (Figure 8). The first prototype was built to validate filament winding techniques for pillow manufacturing. The second prototype has an improved winding pattern, with reinforced corners. Pillow segments cannot be tested individually, because pressure elimination in the flat surfaces is necessary for this concept to work. Since the elliptical end pieces have not been built, the pillow segments were tested between parallel steel plates that control the bending stresses in the flat ends (Figure 8) in a manner equivalent to having the full set of pillow segments and elliptical ends. The first prototype failed at a corner when the pressure reached 60 atm. The second prototype was pressurized to 120 atm with no structural failure. However, the vessel leaked through the boss, making it impossible to complete the burst test. Future tests will correct boss leaks and determine the structural and packaging merits of this vessel design.

Figure 8. Prototype pillow vessel segment (left) and pillow vessel segment being pressure tested between steel plates (right).

Macrolattice Conformable Vessels: This second approach to conformability uses an internal structure to hold the vessel together and reduce the bending stresses on the outer skin of the vessel. The vessel can then be designed with a thin outer skin that is designed for hydrogen containment only.

The internal structure in a macrolattice vessel consists of struts made of steel or composite materials that work only under tension (for optimum structural efficiency). The geometrical pattern of the struts was obtained from the crystallography tables [10], by determining which of all the available lattices yields optimum performance. The selected lattice has high volumetric efficiency (over 80% without including the outer skin) and manufacturability (only two struts cross at any given point). This concept was used for building and testing the first ever macrolattice conformable container (Figure 9a). This is a cubic container with polycarbonate surfaces held together by metallic struts. The container was pressure tested in our high pressure laboratory up to 30 atm. At this pressure, the plastic edge seal located between the square faces lost its position in its groove, allowing the air in the vessel to leak. No structural failure was observed. This is an encouraging result, considering that future generations of macrolattice vessels will not use plastic seals.



(a) (b)

Figure 9. Two approaches for building internal vessel structures for conformability. (a) Macrolattice vessel. (b) replicant structure.

Replicant Conformable Vessels: Replicant vessels also use an internal structure to hold the pressure, along with a thin outer skin that contains the hydrogen. The internal structure is made of “replicants,” which are small structural members that fill the interior of the vessel (Figure 9b). It is believed replicant vessels will have a mass production advantage for large sizes (e.g. delivery trucks for pressurized hydrogen) where individual macrolattice struts would be very large. Mass production of the replicants and robotic assembly could result in large scale vessels with reduced manufacturing costs that would be time consuming to produce by conventional methods (filament winding).

CONCLUSIONS

This paper has described ongoing work at LLNL on high performance storage vessels for (L)H_2 automobiles. We are developing and demonstrating cryogenic compatible vessels that can utilize the high density of LH_2 while virtually eliminating evaporative losses. Insulated pressure vessels are versatile, enabling vehicles to use cryogenic and/or ambient temperature hydrogen. This flexibility provides advantages with respect to conventional storage technologies. Insulated pressure vessels are more compact than ambient temperature pressure vessels, and have lower energy intensity and evaporative losses than conventional LH_2 tanks. These advantages likely outweigh the additional cost of a high pressure vessel and cryogenic insulation. Aluminum-lined, composite wrapped pressure vessels have been successfully used for insulated pressure vessels, even though they are not designed for cryogenic operation. Multiple tests have been carried out to evaluate their safety. All experiments and analysis to date indicate that cryogenic operation does not weaken the pressure vessels. Insulated pressure vessels have been tested extensively and now successfully demonstrated onboard a vehicle. We are now working on a third generation of insulated pressure vessel with much improved packaging characteristics.

We are also designing and testing conformable pressure vessels for optimum utilization of the space available in the vehicle. We are developing three approaches to conformability: filament wound, macrolattice and replicant vessels. Filament wound vessels are designed with an appropriate geometry that effectively cancels the forces caused by internal pressure, thereby holding the bending stresses that characterize conformable pressure vessels to a manageable level. We have built and pressure tested two filament-wound conformable vessel prototypes, and further testing is planned to determine the feasibility of this approach. Macrolattice pressure vessels consist of an internal structure surrounded by an outer skin. The internal structure is designed to resist the stresses caused by the internal pressure, and is made of struts arranged in a pattern inspired by the crystallography tables. Under this configuration, struts are structurally efficient (working under pure tension) and bending stresses in the outer skin are kept at a manageable level by using a small cell size (2 cm or less). A thin outer skin can then be designed for hydrogen containment only. We have built and pressure tested the first macrolattice vessel prototype, and future generations are planned for improved performance. Finally, replicant vessels are made of an internal structure made of small components that are bonded into an internal structure with a thin outer containment skin. Replicant vessels are most appropriate for large sizes where conventional techniques may be difficult to apply.

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